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Isopiestic Kinetics of Powdered Pd/C/DPB Composite

Long Dinh and Andrew Saab

1.1 Introduction

In a 2006 LLNL internal report, a study of DEB and DPB based hydrogen getter materials was described¹. The materials, consisting of DEB or DPB physically blended with amorphous carbon on which palladium nanoparticle catalyst was supported, were studied during the course of reaction with fixed aliquots of hydrogen gas in order to observe their hydrogen consumption capacities as a function of ambient hydrogen pressure. The experiments demonstrated that the getter capacity was directly proportional to hydrogen fugacity: the lower the initial hydrogen pressure, the lower the resultant capacity at correspondingly low steady-state pressures. In the course of these experiments, further interesting observations were made of DEB and DPB reduction by hydrogen gas that painted a picture of a complicated reaction mechanism. To summarize, it was determined that reaction rate was controlled partly by diffusion of the organic diacetylene toward the catalyst surface. The results indicated this diffusion was in turn enhanced by phase changes in the course of the reaction that result in a liquid phase of the getter, and also by the heat of reaction, itself being proportional to initial reaction rate. However, these same two terms were speculated to have negative impacts on the net reaction kinetics, as well. It was suggested the liquid phase served to block gas access, and that excessively fast initial rates limited rate and capacity at later times by creating a depletion zone of reactant around the catalyst.

Because of the nature of the experiments, whereby both hydrogen pressure and getter activity were changing in time, actual kinetic information could not be gathered. Knowledge of the reaction rate characteristics of these materials as a function of pressure and temperature is crucial to understanding the overall behavior of this material in service. Further, direct observation of the reaction rate can permit estimates of the diffusion of the reactive species. The present work centers on the development of an understanding of the kinetics for the hydrogenation of DPB and DEB as a function of temperature and pressure.

1.2 Experimental Approach or Methodology

In order to provide direct information on kinetics, the experimental apparatus described in 2006¹ required modification such that the thermodynamic activity of only a single reactive species in the system would be allowed to change, i.e., either hydrogen fugacity or getter activity must remain fixed. Clearly, because it is the getter that is the functional compound in actual use, it is the hydrogen fugacity that should be held constant. This was most directly done by use of a pressure-feedback mass-flow controller. The hydrogen pressure (fugacity) served as a system feedback set point, with flow as the parameter adjusted to maintain the set point during consumption of the gas by the getter. Consequently, the measurement of flow in time was identically the reaction rate. The system previously used was rebuilt to accommodate a Model 649 pressure-set point

mass-flow controller from MKS instruments. The controller had a pressure measurement range of 10 Torr, and a minimum mass flow measurement range of 0.1 sccm. Tests of the instrument, however, revealed that the system was capable of controlling to

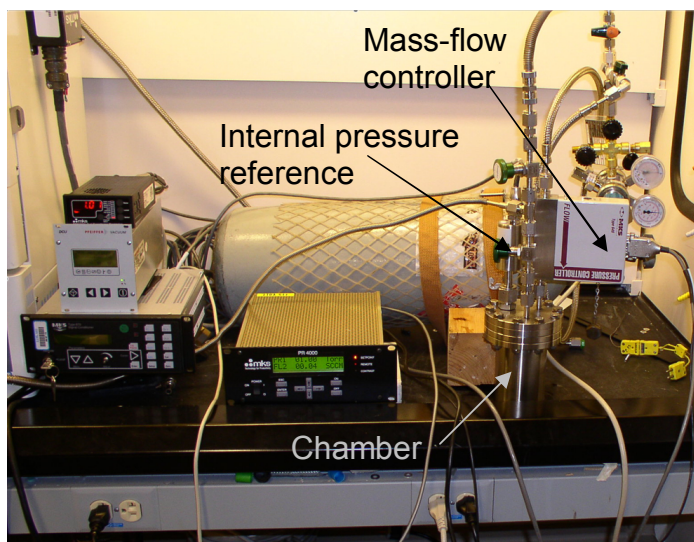


Figure 1. Isopiestic hydrogen reactor

approximately 0.02 sccm. The assembled system is illustrated in figure 1. In a typical experiment, approximately 400 mg of getter material was placed in a small (~20 mL) beaker. This beaker was in turn placed inside a 60 mm crystallizing dish, which was filled with approximately 2.8 g of activated carbon sorbent. The carbon served two purposes. First, it acted as a sorption trap for volatile organics liberated during the hydrogenation reaction, with the goal of reducing any pressure offset due to the evolution of such species. Second, the carbon could be analyzed post reaction to determine the nature of the volatile compounds created during the reaction. This second point relates not only to the reaction mechanism, but also to material lifetime and compatibility in deployment.

The system was calibrated and tuned by installing in front of the main shutoff valve a leak valve, through which the main reaction vessel could be vacuum pumped in order to simulate the consumption of hydrogen by reactive getter. Hydrogen was fed to the MFC as in an actual experiment, and the feedback controller was set to maintain a given pressure within the anticipated range. The model 649A is a proportional/integral controller. Perhaps because of the lack of feedback on the derivative of the error signal (which is to say, the 649A is not a PID controller), the best tuning for the required operation resulted in the unusual case of most of the control being maintained by the integral term.

For the initial round of experiments, DPB combined with Pd/C catalyst was subjected to 1 Torr, 2 Torr, 4 Torr, and 8 Torr of H_2 pressure. Data as pressure and flow in time were collected on a PC with a 12-bit DAC card. Total run times ranged from 4 to 7 days. Sample data collection rate was intended to be 0.5 Hz, but due to a manual settings error in the collection software, the actual rate was 50 Hz. This was not evident during

collection since the on-screen data display updates at an apparent 0.5 Hz, even though the actual collection is considerably faster. The resulting data sets after collection were thus extremely large. Therefore, for purposes of manageability, only data up to the first 24 hours from each experiment was extracted and processed for fitting.

Because the 649A is a duty cycle (i.e. closed loop) and not an open-loop controller, the collected mass flow data was in the form of closely spaced narrow flow spikes typically on the order of 0.1 sccm magnitude above the baseline. Figure 2 shows a plot of typical raw data. Owing to the accidentally large amount of data and to the duty cycle nature of the controller, data were processed for fitting by first performing a weighted least-squares fit on the total set, then fitting the result with a cubic spline. The least-squares fit served to smooth the data, while the spline reduced the data set by orders of magnitude. All data manipulations were performed in Kaleidagraph.

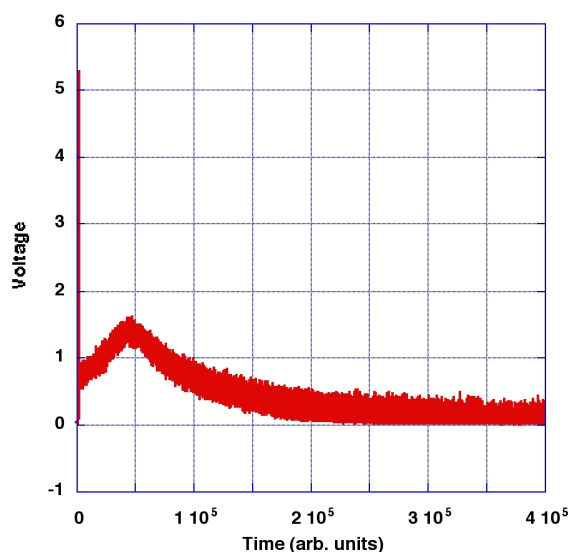


Figure 2. Raw flow data as voltage vs. time

1.3 Results and Discussion

The reaction rate vs. time data for constant pressures at 1 Torr, 2 Torr, 4 Torr, and 8 Torr are presented in figure 3. The first notable feature of all the data is the prominent peak in the mass flow, and therefore in the reaction rate, in the relatively early parts of the reaction. The time position and breadth of this increase was inversely proportional to hydrogen pressure. As pressure increased, the rate peak narrowed and moved to shorter times.

At times following the initial rate increase, the situation became much more complicated, depending on both time and hydrogen activity. In the simplest case, which was at 8 Torr, the reaction rate decayed monotonically after the initial rate peak. In contrast, at 2 and 4 Torr a second significant increase in the reaction rate was visible. Also, a third, less prominent increase in the rate was visible at both 1 and 2 Torr, occurring relatively soon after the first large rate increase. As with the first large rate increase, the onset times of

these secondary increases decreased with increasing hydrogen pressure. It is necessary to point out that for the 1 Torr experiment the controller required retuning after approximately 15 hours of run time. The data just prior to retuning was showing increasingly large swings in flow rate, indicating a possible oscillation. However, the time at which this oscillation occurred roughly corresponded to the time at which the second rate increase peak (as seen at 2 Torr and 4 Torr) should have been observed, given the trend from the 2 Torr and 4 Torr experiments. Thus, it is possible that the wide flow swings concealed the same flow rate increase observed at 2 and 4 Torr.

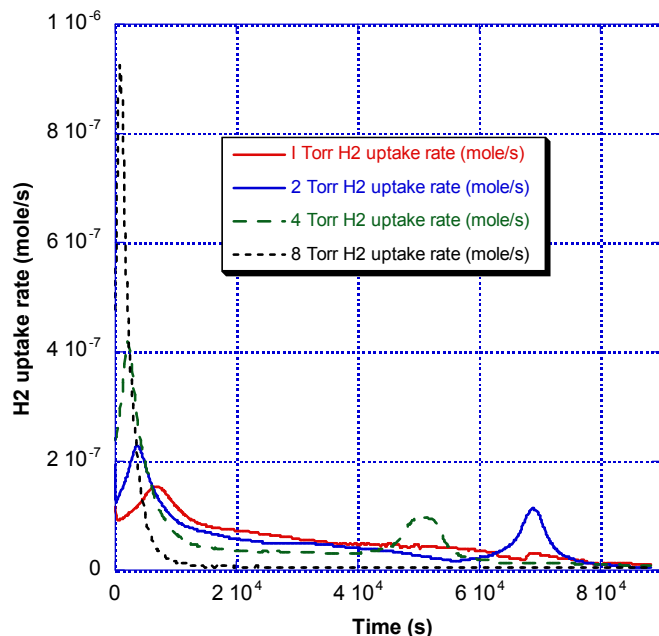


Figure 3. Reaction rate vs. time for hydrogenation of DPB on Pd/C powder

Figure 4a recasts the data in terms of reacted fraction, α , which is the integrated form of the instantaneous kinetics of figure 2. In all cases, the reaction progress generally follows a sigmoidal shape. The sigmoidal shape is commonly seen in solid-state reactions that undergo a nucleation-and-growth reaction pattern², suggesting that as the reaction proceeds around a catalyst site, at some critical reacted volume the reaction rate speeds up owing to enhanced reactant transport. This is consistent with the speculation from earlier work that liquefaction of the getter as a function of hydrogen saturation enhances the reaction rate by improving the diffusional kinetics of unreacted material toward the catalyst¹.

In order to evaluate the reactant diffusion coefficient, multiple fits to early time regions of the data (those ranging from the first to the second inflections of the first sigmoid) were attempted using simple single-component-diffusion reaction models². However, these proved fruitless, indicating that even in the relatively well-behaved portion of the data the mechanism is quite complex, and probably consists of a convolution of multiple rate controlling terms. Further deviation from any easily interpretable case is evident

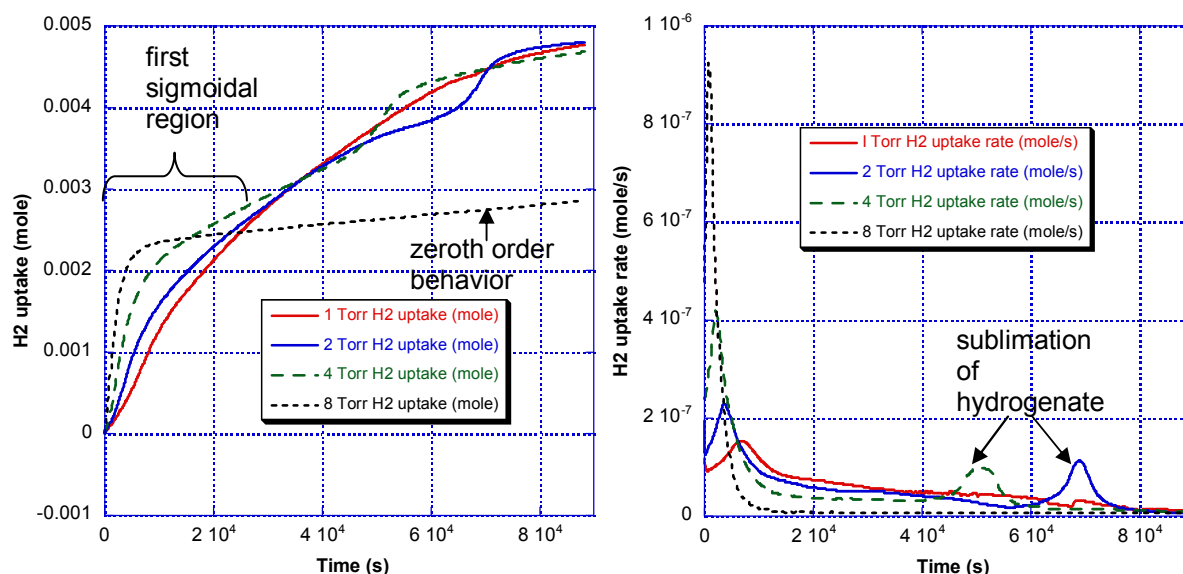


Figure 4. a) Integrated kinetics (uptake vs. time) for DPB/Pd/C hydrogenation b) Instantaneous kinetics for the same reaction

when the net reaction progress in time is considered as a function of pressure. The 1, 2, and 4 Torr cases all reach approximately 80% capacity after 24 hours. In contrast, the 8 Torr material achieves only about 40% reaction. For a well behaved gas/solid reaction at a given extent of reaction and temperature the relationship $P_1 t_1 = P_2 t_2$ holds. Clearly, for DPB on Pd/C, it does not. Further, the linear region of the 8 Torr data at later times indicates that the reaction becomes zero order ($\alpha = kt$); this is consistent with the previously proposed depletion area around the catalyst formed due to the high initial reaction rate. Once the zone forms, the DPB activity on the bulk side (away from the catalyst) is essentially uniform in time provided the diffusion rate across the zone is small. This in turn implies that diffusion of reactant to the catalyst is independent of time during the period of observation. Thus, the reaction appears to obey zeroth order kinetics.

Turning again to the instantaneous rate data in figure 4b, the last outstanding features to be considered are the accelerations of rate at later times for all cases except for the 8 Torr result. Similar results have been observed for the hydrogenation rate of DPB/Pd/C pellets. This has been attributed to the formation of a solid phase of hydrogenated DPB following liquefaction³, which acts as a hydrogen barrier and which must be given time to sublime away before the reaction rate increases.

1.4 Conclusion

Evidently, the DPB/Pd/C powder system cannot be modeled with a gas diffusion process such as that of DPB/Pd/C pellets³; neither does it follow simple diffusional models for typical powder solid/gas reactions. Consistent with prior observations, this system's mechanism is complex. The present work also supports in more detail prior assessments of certain characteristics of the reaction mechanism, namely the impact of reaction rate on ultimate capacity, and the importance of phase changes in mediating the achievable rate. The implications of this behavior are certainly greatest for any application that uses

the powdered form of this material instead of the pelletized version. The next steps in developing an understanding of the basic DPB/Pd/C behavior will be to perform chemical analysis of the activated carbon sorbent and of the reaction headspace in order to develop a profile of volatile substances, and also to perform temperature dependent measurements over the same range of pressures explored in this report. The temperature dependence will be important in developing the concepts of thermal feedback into the reaction mechanism as a function of initial rate. It may also allow for the determination of basic thermodynamic parameters such as activation energy.

1.5 References

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